

Appendix B

Equations Used in Major Codes

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B. GOVERNING EQUATIONS USED IN MAJOR CODES

B.1 INTRODUCTION

This section briefly summarizes the equations used in the major computer codes. More information can be found in the user's manual for each of the codes:

- STOMP White and Oostrom 1999.

B.2 FLOW AND TRANSPORT

B.2.1 Overview

This section discusses the equations important in calculating moisture flow and contaminant transport. All three major codes use the same basic equations. The first section presents the equations on which the water flow calculations are based. The next section discusses contaminant transport associated with moisture flow. The final section describes moisture movement under diffusive conditions.

B.2.2 Moisture Flow

Two distinct moisture content regimes are present during contaminant transport: the unconfined aquifer and the disposal facility/vadose zone. In the unconfined aquifer all the pore spaces are filled with water; that is, the medium is saturated with water. In the disposal facility/vadose zone the pore spaces between the soil particles are only partially filled with water. These zones are unsaturated.

Water flow through a saturated porous medium, such as the unconfined aquifer, is governed by the empirical relationship known as Darcy's Law (Freeze 1979) and by the conservation of mass. Darcy's law can be expressed as

$$\Rightarrow \Leftrightarrow \Rightarrow$$

$$\mathbf{v} = -\mathbf{K} \nabla h \quad (\text{C.1})$$

where \mathbf{v} is the velocity vector (m/year)
 \mathbf{K} is the hydraulic conductivity tensor (m/year)
 h is the hydraulic head vector (m).

By using the conservation of water entering and leaving a volume and by using Darcy's law to relate the hydraulic gradient to the rate at which water enters and leaves the same volume, transient water flow in a saturated porous media can be expressed as

$$\nabla \left[\frac{\partial}{\partial t} \nabla h \right] = \frac{Sh}{t} + Q \quad (C.2)$$

where S is the specific storage (m^{-1})

Q is the source or sink of moisture (y^{-1}).

Darcy's law defines the discharge of water through a cross section of porous media. However, in contamination transport, the average velocity of water flowing through the medium is important. This is because contaminants that are not geochemically retarded move with the water. The average velocity of the pore water is determined by dividing the velocity of the water by the porosity of the medium. Porosity is defined as the ratio of void space to total volume.

In an unsaturated medium, the pores are not completely filled with water. Capillary forces and the dependence of hydraulic conductivity on moisture content also must be considered. Richards equation (Richards 1931) becomes the governing equation:

$$\nabla [K(\psi) \nabla \psi] + \partial K_{zz}(\psi) / \partial z = (d\theta/d\psi) (\partial \psi / \partial t) + Q \quad (C.3)$$

where K is again the hydraulic conductivity tensor (m/year), but now depends on the pressure head

ψ is the pressure head (m), which depends on the moisture content

θ is the moisture content (dimensionless)

z is the vertical column of moisture (m).

The relationship between the pressure head and the hydraulic head is simply

$$h = \psi + z. \quad (C.4)$$

For the performance assessment calculations, the hydraulic conductivity tensor is reduced to a single function, with

$$K_{ij} = K, \text{ for } i = j \text{ and} \quad (C.5)$$

$$K_{ij} = 0, \text{ for } i \neq j.$$

The functional dependence of the pressure head on moisture content and of the hydraulic conductivity on pressure head and ultimately on moisture content is discussed in Section 3.4.3.2.

For extremely dry conditions, vapor diffusion may be important. In such conditions, water does not move as a collective body, but rather as single molecules. Such diffusion can be described by Fick's equation,

$$\frac{dm}{dt} = -D_v A \frac{dC}{dx} \quad (C.6)$$

where dm/dt is the mass rate of water vapor diffusion (g/year)

- D_v is the effective vapor diffusion coefficient (m²/year)
 A is the cross section area (m²)
 C is the water vapor mass concentration in the gas phase (g/m³)
 dC/dx is the water vapor mass concentration gradient (g/m⁴).

B.2.3 Advective and Diffusive Transport

The equation for the advective and diffusive transport of contaminants can be viewed as a mass balance on a differential volume. The advective-dispersive equation for solute movement through a porous medium with a constant, steady-state flow velocity was developed (Codell 1982) for the limiting case of unidirectional advective transport with three-dimensional dispersion in a homogeneous, saturated aquifer,

$$\begin{aligned}
 n_e \frac{\partial C}{\partial t} + (n - n_e) \frac{\partial G}{\partial t} + (1 - n) \frac{\partial P}{\partial t} + n_e u \frac{\partial C}{\partial x} = \\
 n_e \left[E_x \frac{\partial^2 C}{\partial x^2} + E_y \frac{\partial^2 C}{\partial y^2} + E_z \frac{\partial^2 C}{\partial z^2} \right] + \\
 (n - n_e) \left[E_x^1 \frac{\partial^2 G}{\partial x^2} + E_y^1 \frac{\partial^2 G}{\partial y^2} + E_z^1 \frac{\partial^2 G}{\partial z^2} \right] - \\
 n_e \lambda C - (1 - n) \lambda P - (n - n_e) \lambda G
 \end{aligned} \tag{C.7}$$

- where C is the dissolved concentration in the liquid phase in voids that are interconnected and allow flow [flowing voids] (g/m³ or Ci/m³)
 G is the dissolved concentration in the liquid phase in voids that are not interconnected and do not allow flow [non-flowing voids] (g/m³ or Ci/m³)
 P is the particulate concentrations on the solid phase (g/g or Ci/g)
 n is the total porosity (dimensionless)
 n_e is the effective porosity (dimensionless)
 t is the time (year)
 u is the x-component of groundwater or pore water velocity (m/year)
 E_i is the dispersion coefficient in the flowing voids in the i-th (where i = x, y, or z) direction (m²/year)
 E_i^1 is the diffusion coefficient in the non-flowing voids in the i-th direction (m²/year)
 λ is the decay constant [= (ln 2)/half life] (y⁻¹).

Each term in the equation represents some aspect of the solute movement through the porous medium. The first term on the left of the equal sign is the accumulation (storage) of the

solute in the liquid phase in the flowing void. The second term is the accumulation in the liquid phase in the nonflowing void. The third term is the accumulation in the solid phase; and the term to the left of the equal sign is x-direction advective transport in the flowing voids in the liquid phase. The first term to the right of the equal sign represents the dispersive transport in the flowing voids in the liquid phase in each direction. The second term represents the diffusive transport in the nonflowing voids in the liquid phase in each direction. The last terms are the chemical degradation or radioactive decay in the liquid phase in the flowing void, in the solid phase, and in the liquid phase in the nonflowing void respectively.

Using the following assumptions:

- The dissolved concentration in the nonflowing voids (G) equals the dissolved concentration in the flowing voids (C) for each time and position
- The contaminant absorption process can be described by a constant, ($K = \rho^* K_d / (1 - n)$), representing the ratio between the contaminant absorbed to the soil matrix (P) and the contaminant dissolved in solution (C)
- The diffusion in the nonflowing void (E'_i) is comparable with the dispersion in the flowing void (E_i), the equation (D.7) can be simplified to

$$\frac{\partial C}{\partial t} + \frac{u}{R_f} \frac{\partial C}{\partial x} = \frac{D_x}{R_f} \frac{\partial^2 C}{\partial x^2} + \frac{D_y}{R_f} \frac{\partial^2 C}{\partial y^2} + \frac{D_z}{R_f} \frac{\partial^2 C}{\partial z^2} - \lambda C \quad (C.8)$$

$$\text{in which} \quad D_i = n E_i / n_e \quad (C.9)$$

$$\text{and} \quad R_f = n / n_e + (\rho^* K_d) / n_e \quad (C.10)$$

and where

D_i is the pseudodispersion coefficient (m^2/year)

R_f is the retardation factor (dimensionless)

ρ is the bulk density (g/m^3)

K_d is the equilibrium (partition or distribution) coefficient (m^3/g).

The retardation factor (R_f) is used as a measure of the mobility of constituents in a porous medium.

By making the following substitutions,

$$u^* = u / R_f \quad (C.11)$$

and

$$D_i^* = D_i / R_f,$$

the contaminant transport equation can be written as

$$\frac{\partial C}{\partial t} + u^* \frac{\partial C}{\partial x} = D_x^* \frac{\partial^2 C}{\partial x^2} + D_y^* \frac{\partial^2 C}{\partial y^2} + D_z^* \frac{\partial^2 C}{\partial z^2} - \lambda C \quad (\text{C.12})$$

The first equation of this section [equation (D.1)] specifically addresses the general conditions for saturated flow and solute movement. However, with the following minor modifications, it also can be applied to the unsaturated zone:

- The porosities (n and n_e) are assumed to be equal to the soil matrix moisture content
- The one-dimensional flow is in the vertical direction.
- For this case, the retardation factor is defined by

$$R_f = 1 + (\rho^* K_d) / \theta \quad (\text{C.13})$$

where θ is the moisture content of the partially saturated zone and dispersion is considered only in the flow direction.

B.2.4 Vapor Transport

Some contaminants may move upward from the disposal facility to the surface because they are in the vapor phase. Such movement is governed by Fick's second law,

$$D \frac{\partial^2 C}{\partial z^2} = \frac{\partial C}{\partial t} \quad (\text{C.14})$$

where

- C is the concentration (g/m³ or Ci/m³)
- z is the distance (m)
- t is time (year)
- D is the diffusion coefficient (m²/year).

The solution for concentration C in the z direction over time t is given by:

$$\frac{C}{C_0} = \text{erfc}\left(\frac{z}{2\sqrt{Dt}}\right) \quad (\text{C.15})$$

where erfc is the complimentary error function and C/C₀ is the relative concentration. The mass transport across the surface becomes

$$\frac{\partial C}{\partial t} = \frac{C_0}{2\sqrt{\pi Dt}} \frac{z}{t} \exp\left(\frac{-z^2}{4Dt}\right) \quad (\text{C.16})$$

B.3 WASTE FORM

ADVECTION-, DIFFUSION-, AND SOLUBILITY-DOMINATED Release Models for Residual Wastes

As discussed in the main text, the source terms for the risk assessment consist of four separate sources that include (a) past leaks and spills, (b) leakage during retrieval, (c) residual waste leachate from the tanks following closure, and (d) residual waste leachate from the tank ancillary following closure. The past leaks represent tank waste that has leaked into the vadose zone and has been migrating through vadose zone for a number of years. Retrieval leakage to the vadose zone refers to waste leakage that could occur during waste retrieval operations using water-based sluicing.

Releases from the residual wastes (both from tank and tank ancillary equipment) in most cases would occur over a long time period following closure of the tank farm when infiltrating water would enter the tank, dissolve contaminants, and migrate contaminants into the vadose zone and to the groundwater. In addition to the scenarios where the release duration is fixed and are defined in the main text as R_0 through R_4 release scenarios (see Appendix A), three additional models –advection-dominated, diffusion-dominated, and solubility-controlled – will be considered. Unlike the R_0 through R_4 release scenarios, release durations for these three models are not fixed a priori. Detailed descriptions on the three models are presented later. First, the conceptual basis and assumptions for the source term release are presented.

B.3.1 Conceptual Model of Source Term Release.

The actual process of contaminant (radionuclides and hazardous chemicals) release for residual wastes from a tank cannot be modeled precisely because of the variability of chemical and physical reactions that occur between the waste material and the infiltrating water. In the real system, contaminants are distributed in a heterogeneous manner within the tank. These contaminants are released into solution at different rates because of the variability in waste material. Finally, variable types and quantities of contaminants are dissolved into the infiltrating water over time, depending on which waste material contacts a particular fluid volume. Therefore, averaging concepts are used in modeling to simplify the mathematical representation of the real system. These concepts must be justified, however, as being a conservative representation of the real system.

The following assumptions are made for the source-term release estimates.

- The release of contaminants from tank residuals is evaluated assuming that the structural integrity of the tanks degrades, allowing recharge (infiltrating) water to enter the tank, and dissolve contaminants from the residuals. The release of contaminants occurs by dissolution of the waste material contaminants into the infiltrating water migrating into and out of tanks through cracks.
- For both stabilized (grouted) and unstabilized (not grouted) residual wastes in tank and tank ancillary equipment, it is assumed that the contaminant inventory will be available for release into the infiltrating solution via an advection-dominated or a diffusion-dominated or a solubility-controlled release model
- Unit quantities are assumed for various modeling runs. Because risk estimates are directly proportional to total inventory, the modeling runs with unit quantities can be scaled to calculate risk for any initial inventory.
- Three radionuclides (i.e., Tc-99, I-129 and U-238) are considered for the three release models (i.e., advection-, diffusion-dominated, and solubility-controlled) described below.
- For those stabilized waste materials that are incorporated into a waste form that controls radionuclide release by diffusion (i.e., grout), it is assumed that the diffusion coefficient remains constant over time for the diffusion-dominated release model.
- Contaminant inventories are assumed to be homogeneously distributed among the wastes. For the stabilized, grouted wastes, it is assumed that the contaminants are uniformly distributed in the residual wastes only in the bottom of the tank.

B.3.2 Mathematical Models of Release Mechanisms for the Advection-, Diffusion-, and Solubility-Dominated Models

As indicated earlier, in addition to the R_0 through R_4 release scenarios (Appendix A), the source terms will be estimated by an alternate advection-, diffusion-, or solubility-dominated release model. The mathematical description and conditions under which the different mechanisms occur are provided in the following sections. The area under each release model equals to unit inventory.

Advection-Dominated Release Model. The advection-dominated release model (mixing-cell cascade model) is used to simulate the processes of releases from stabilized (grouted tank or tank ancillary) wastes. For stabilized wastes, the radionuclides exit the facility at a rate determined by the flow of water and the amount of dispersion (mixing) within the tank. The mixing-cell cascade model (Kozak et al. 1990; Wood et al. 1995) is based on the dispersion analysis of chemical reactors and allows the analysis to incorporate the effects of dispersion in the tank in a simplified manner. In this model, the tank inside is considered to be composed of a cascade of N equal-sized, well-stirred cells in series. The total volume of the N cells is equal to the volume of the tank residual waste.

$$Q(t) = q A C_o e^{-\alpha Nt} \sum_{n=1}^N \frac{(\alpha Nt)^{n-1}}{(n-1)!}$$

The mixing-cell cascade model for N equal-sized cells is described by the following equation:

where:

Q = release rate (Ci/yr)

q = vertical Darcy flux (m/yr)

A = horizontal (planar) area of the tank inside

$\alpha = q/(\theta dR)$

θ = volumetric moisture content in the residual waste

d = vertical depth of the residual waste material (m)

R = retardation factor in the waste material (assumed R=1).

The initial concentration of contaminant in the interstitial water can be determined from the following equation:

$$C_o = \frac{m}{\theta VR}$$

where m equals total facility inventory (assumed unity) of the radionuclides in the tank and V equals total volume of the residual waste (i.e., 360 ft³ or 1% residual following TPA goal). The spatially variable velocities, V, and moisture contents, θ , which are obtained via flow modeling within the tank, will be used to determine C_o . Note that all simulation runs except for Cases 11 and 12 use backfill as the tank fill material. Cases 11 and 12 use grout as the tank fill material.

The mixing-cell cascade model provides results equivalent to the one-dimensional, convective-dispersion equation with varying values of the dispersion coefficient (Kozak et al. 1990). In the limit, as N approaches infinity, the model represents flow through a system with zero dispersion, whereas for N equal to one, the model represents flow with an infinite dispersion coefficient. A value of N = 10 will be used reflecting moderate dispersion.

Diffusion-Dominated Release Model. The diffusion-dominated release model is used to simulate the release of contaminants from stabilized (e.g., grouted tank or tank ancillary) wastes. In the absence of little or no advection through the waste container, the release can be modeled as a diffusion-limited process. The diffusion from cylindrical containers leads to an expression for flux that contains infinite series (Kozak et al. 1990). The series converges slowly for small diffusion coefficients for short times, and even for relatively long times. As a result, a one-dimensional diffusion solution can be adopted (Crank 1975). The solution, for a semi-infinite medium with the concentration C_0 throughout, initially, and with zero surface concentration, is given by

$$C = C_0 \operatorname{erf} \frac{x}{2\sqrt{(D_e t)}}$$

where:

erf = standard error function,

D_e = effective diffusion coefficient of the radionuclides in the waste form, and

t = time.

The rate of loss of diffusing substance per unit area from the semi-infinite medium when the surface concentration is zero, is given by:

$$(D_e \frac{\partial C}{\partial x})_{x=0} = C_0 \sqrt{\frac{D_e}{\pi t}}$$

The above equation has the form of diffusion mass transfer based on leaching theory. This simplified release model leads to the following form:

$$q = A C_0 \sqrt{\frac{D_e}{\pi t}}$$

where:

q = release rate from a single waste cell (Ci/yr),

A = effective surface area of a single cell, and

C_0 = concentration in a cell.

Because the residual waste is likely contained in various cells with differing sizes and shapes, the diffusive release rate, Q , from all residual waste in the tank can be determined by the following equation:

$$Q = C_0 \sqrt{\frac{D_e}{\pi t}} \sum_{i=1}^n A_i$$

$$= C_0 A_t \sqrt{\frac{D_e}{\pi t}}$$

where n is the number of cells, A_i is the surface area of individual cells and A_t is total surface area of a tank.

By assuming that the cells are constant, i.e.,

$$I = C_0 \sum_{i=1}^n V_i = C_0 V_t$$

where I is the total inventory, V_i is the volume of i -th cell and V_t is the total volume of all cells.

Combining preceding equations, we obtain:

$$Q = I \frac{A_t}{V_t} \sqrt{\frac{D_e}{\pi t}}$$

The ratio A_t/V_t can be replaced by a ratio of a surface area over volume of a tank (only the portion of the tank containing waste will be used to obtain the ratio).

The model calculation is conservative in two aspects. First, the surface area of a tank might not be completely exposed to a moving stream of water. Second, the radionuclides reaching the tank surface area are assumed to be released into the water stream and instantaneously reach the bottom of the tank for release. Two different diffusion coefficient values will be used: 6×10^{-7} cm²/sec based on Kincaid et al. (1995) and 5×10^{-8} cm²/sec based on *Hanford Waste-Form Release and Sediment Interaction* (Serne and Wood 1990).

Solubility-Controlled Release Model. Solubility-controlled release models assume that a known solid is present or rapidly forms, and controls the solution concentration in the aqueous phase of the constituents being released. Solubility models are thermodynamic equilibrium models and do not consider kinetics (time required to dissolve or completely precipitate) (Serne and Wood 1990). When identification of the likely controlling solid is difficult, empirical solubility experiments are performed to gather data that can be used to generate an empirical solubility release model. Such empirical models assume a controlling solid and fix the chemistry of all constituents to derive a fixed value for the concentration of specific contaminants. No solubility empirical models presently exist for modeling contaminants from residual tank wastes. However, a solubility-controlled release model (i.e., "cake" model) has often been postulated in previous risk assessments.

The cake model consists of a very simple mathematical formulation containing a recharge rate term, a term for waste solid solubility, and a term for the cross-sectional area of the waste source (i.e., single-shell tank footprint).

The contaminant release mechanism of the cake model is the dissolution of the "structural matrix." As the matrix dissolves, all the contaminants are assumed to leach congruently at the same rate. When applied to the residual tank wastes, the term "cake" applies to the sludge and hard heel residual in the tanks, which compose the "structural matrix." The release rate for a given contaminant (Tc-99, I-129 and U-238) is given by:

$$dM / dt = -M_o A Q_w C_{wo}^{sol} / M_{wo}$$

where M_{wo} = the original mass of cake (kg). M_{wo} can be derived by the product of tank waste volume (TPA goal of 99% removal) and waste density (1.7 g/cm³),

M_o = the original quantity of the contaminant in C_i embedded in the cake,

M = $M(t)$ is the current quantity of the contaminant contained in the cake (C_i or kg) at time t ,

A = the surface area of the cake exposed to the release mechanism,

C_{wo}^{sol} = the aqueous solubility of the cake simulated as a nitrate salt; the concentration most commonly used is 360 g/L. Based on expected waste characteristics, a value of 72 g/L will be used.

Q_w = the recharge rate in cm/yr, also termed "infiltration rate," and

dM/dt = the rate of loss of contaminant from the cake waste form per unit time t (the rate at which the contaminant enters the vadose zone).

Recharge rates for the cake model are listed in Table I in the main text. Cross-sectional footprint for the cake model consists of the individual tank area.

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